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<p>(54) Title: RADIATION-CURABLE RESIN COMPOSITION</p> <p>(57) Abstract.</p> <p>Disclosed is a radiation-curable resin composition which is suitable for use as a coating material for optical fiber, especially as a primary coating material for radiation fiber which has high breaking strength while it has a low modulus of elasticity. The radiation-curable resin composition comprises (A) a polymer having 1.2 or more polymerizable unsaturated groups in average in one molecule, a urethane bond in a molecular chain, and a number average molecular weight of 3,000-30,000; (B) a poly-functional monomer having a plurality of polymerizable unsaturated groups; (C) a monomer having one polymerizable unsaturated group; and (D) a radiation-active initiator.</p>		

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RADIATION-CURABLE RESIN COMPOSITION

5 The contents of Japanese Application No. 97-235449, filed August 15, 1997 is hereby incorporated in its entirety by reference.

Field of the Invention

10 The present invention relates to a radiation-curable resin composition, and, especially to a radiation-curable resin composition that is suitable as a coating material for substrates, in particular optical fibers.

15 **Background of the Invention**
Optical fibers, especially, optical glass fibers, are fragile and easily damaged and hence these are coated with a coating material. The properties, 20 specifically, the modulus of elasticity and the like of a coating film made of, for example, a UV-ray curable resin have a great influence on the transmission performances of optical fibers. When optical fibers are coated with a primary coating material having a high

25 modulus of elasticity, the transmission loss of the optical fibers increases because of high lateral pressure. A material having a low modulus of elasticity is, therefore, desirable as the primary coating material. However, conventional coating materials 30 having a low modulus of elasticity have the drawbacks that these materials have generally low breaking

strength and are hence fragile. Specifically, it is desired that the modulus of elasticity of the primary coating material for optical fibers be 0.15 kg/mm^2 or less in terms of secant modulus prescribed in JIS K7127 to absorb high lateral pressure. However, the breaking strength of cured products having such a low modulus of elasticity is as low as 0.15 kg/mm^2 or less in terms of the tensile strength at break prescribed in JIS K7127. The products thus exhibit only poor practicability.

10 An object of the present invention is to provide a radiation-curable resin composition which is suitable for use as a substrate coating material, in particular, an optical fiber coating material, and, more particularly, as a primary coating material for 15 optical fibers which has a high breaking strength while exhibiting a low modulus of elasticity.

Summary of the Present Invention

Accordingly, the present invention provides 20 a coated optical fiber comprising:
a coating having,
a tensile strength at break of more than 0.15 kg/mm^2 ,
and
a secant modulus of 0.15 kg/mm^2 or less.

25 Furthermore, the present invention provides a radiation-curable resin composition, comprising:
(A) a polymer composition having 1.2 or more polymerizable unsaturated groups on average in one molecule, urethane bonds in a molecular chain, and a
30 number average molecular weight of 3,000-30,000;
(B) a poly-functional monomer having a two or more polymerizable unsaturated groups;

(C) a monomer having one polymerizable unsaturated group; and

(D) a radiation-active initiator, wherein the radiation-curable resin composition is irradiated with 5 ultraviolet light in air at a dose of 1 J/cm² to provide a cured product having at a thickness of 200 µm a secant modulus of 0.15 kg/mm² or less and a tensile strength at break of more than 0.15 kg/mm².

10

DETAILED DESCRIPTION OF THE INVENTION

AND PREFERRED EMBODIMENTS

The composition of the present invention will now be explained in detail by way of a preferred embodiment. Herein certain terms, unless otherwise specified, are understood to used refer to certain chemical groups and compounds. These terms are defined below.

"(meth)acrylic acid" refers to substituted and unsubstituted acrylic acid, methacrylic acid and 20 mixtures thereof, with unsubstituted (meth)acrylic acid being preferred;

"(meth)acryloyl group" refers to a substituted and unsubstituted acryloyl group, methacryloyl group and mixtures thereof, with the unsubstituted (meth)acryloyl 25 group being preferred;

"(meth)acrylate" refers to substituted and unsubstituted acrylate, methacrylate, and mixtures thereof, with unsubstituted (meth)acrylate being preferred.

30

Component (A)

Component (A) is a polymer composition comprising one or more types of polymers (having urethane bonds in a molecular chain and a number 5 average molecular weight of 3,000-30,000) such that the total polymers present have on average 1-2 or more polymerizable unsaturated groups per molecule. The polymerizable unsaturated group in the present specification is a radical polymerizable ethylenically 10 unsaturated group include, for example, (meth)acryloyl and (meth)acrylate groups. The average number of polymerizable unsaturated groups per polymer molecule in the polymer composition selected for component (A) is 1.2 or more, preferably from 1.2 to 4, and 15 morepreferably from 1.5 to 2.5. The number of the polymerizable unsaturated groups contained in each molecule of the polymer may be one or two or more. However, it is necessary that the average number of the polymerizable unsaturated groups in the total component 20 (A) is 1.2 or more per molecule. If the average number of the polymerizable unsaturated groups is less than 1.2 per molecule, only insufficient curing of the composition is obtained. On the other hand, if the average number is too high, an excessive cross-linking 25 reaction is caused, whereby the cured product tends to be fragile.

The number average molecular weight of the polymer is from 3,000 to 30,000, and preferably from 5,000 to 20,000. If the number average molecular weight 30 is less than 3,000, the elongation of the resulting cured product decreases, which causes the tenacity to

decrease easily and tends to produce a transmission loss of optical fiber when the composition is used as a coating material for optical fibers. On the other hand, if the number average molecular weight exceeds 30,000, 5 the viscosity of the resulting composition becomes too large, making it difficult to handle the composition with ease.

The polymers useful in polymer composition of component (A) includes those which contain two or 10 more urethane bonds, and preferably 2-10 urethane bonds. If the number of urethane bonds is less than two, the tenacity of the resulting cured product decreases, which tends to produce a transmission loss of optical fiber when the composition is used as a 15 coating material for optical fibers.

In the polymer composition which is component (A), there are the above limitations to the number of the polymerizable unsaturated groups, the number of urethane bonds, and the number average 20 molecular weight. However, the principal chain of suitable polymers should have a structure constituted of a wide variety of polymer backbones including a polyether polyol urethane-based polymer, polyester polyol urethane-based polymer, polycaprolactone polyol 25 urethane-based polymer, or the like. These polymers may be used either singly or in combinations of two or more. It is especially desirable that the component (A) contain a polyether polyol urethane-based polymer. In this case, either all or a part of the component (A) 30 may be a polyether polyol urethane-based polymer.

The polymer used as the component (A), which is composed of a polyether polyol urethane-based polymer as a basic structure, is produced by reacting (a) a polyether polyol (hereinafter called "polyether polyol (a)") obtained by a ring-opening reaction of an alkylene oxide, (b) a polyisocyanate (hereinafter called "polyisocyanate (b)"), and (c) a compound (hereinafter called "compound (c)") containing both of active hydrogen capable of reacting with the isocyanate group and a polymerizable unsaturated group.

The above polyether polyol (a) is a polyol possessing a polyoxyalkylene structure composed of a polyoxyalkylene group having 2-10 carbon atoms as a repetitive unit and is preferably a diol.

Given as examples of diols possessing the above polyoxyalkylene structure are polyglycol compounds such as polyethylene glycol, polypropylene glycol, polytetramethylene glycol, polyheptamethylene glycol, polyhexamethylene glycol, polydecamethylene glycol, and the like; and polyether diols obtained by ring-opening copolymerization of two or more ionic polymerizable cyclic compounds.

Examples of ion-polymerizable cyclic compounds include cyclic ethers such as ethylene oxide, propylene oxide, butene-1-oxide, isobutene oxide, 3,3-bischloromethyl oxetane, tetrahydrofuran, 2-methyl tetrahydrofuran, 3-methyl tetrahydrofuran, dioxane, trioxane, tetraoxane, cyclohexene oxide, styrene oxide, epichlorohydrin, glycidyl methacrylate, glycidyl acrylate, allyl glycidyl ether, allyl glycidyl carbonate, butadiene monoxide, isoprene monoxide, vinyl

oxetane, vinyl tetrahydrofuran, vinyl cyclohexene oxide, phenyl glycidyl ether, butyl glycidyl ether, and glycidyl benzoate, with cyclic ethers such as ethylene oxide and tetrahydrofuran.

5 Also, polyether diols produced by ring-opening copolymerization of the above ion-polymerizable cyclic compound and a cyclic imine such as ethylene imine or the like, a cyclic lactone such as p-propiolactone or glycolic acid lactide or the like, or 10 cyclic siloxane such as dimethylcyclopolsiloxane or the like can be used.

15 Examples of the specific combinations of two or more ion-polymerizable cyclic compounds include combinations of tetrahydrofuran and propylene oxide, tetrahydrofuran and 2-methyl tetrahydrofuran, tetrahydrofuran and 3-methyl tetrahydrofuran, tetrahydrofuran and ethylene oxide, and propylene oxide and ethylene oxide. Two or more ion-polymerizable cyclic compounds may be combined at random in the 20 resulting ring-opening polymer.

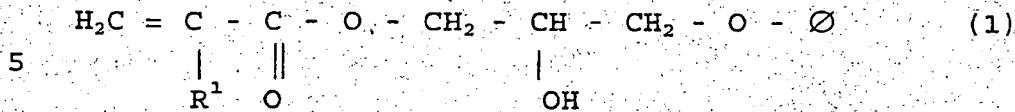
The aforementioned diols having a polyoxyalkylene structure are commercially available under the trademarks, for example, PTMG1000, PTMG2000 (manufactured by Mitsubishi Chemical Corp.), PPG1000, 25 PPG2000, EXCENOL2020, EXCENOL1020 (manufactured by Asahi Oline Co., Ltd.), PEG1000, Unisafe DC1100, Unisafe DC1800 (manufactured by Nippon Oil and Fats Co., Ltd.), PPTG2000, PPTG1000, PTG400, PTGL 2000 (manufactured by Hodogaya Chemical Co., Ltd.), and the 30 like.

In the foregoing production, a diol having no polyoxyalkylene structure and/or a diamine may be used in combination with the polyether polyol (a). Here, as examples of a diol having no polyoxyalkylene structure, a polyester diol, polycaprolactone diol, polycarbonate diol, and the like are given. Examples of a polyester diol include polyester diols obtained by reacting polyhydric alcohol such as ethylene glycol, propylene glycol, tetramethylene glycol, 1,6-hexane diol, neopentyl glycol, or 1,4-cyclohexanedimethanol with a polybasic acid such as phthalic acid, isophthalic acid, terephthalic acid, maleic acid, fumaric acid, adipic acid, sebacic acid, or the like. Examples of a polycaprolactone diol include 15 polycaprolactone diols obtained by reacting ϵ -caprolactone diol with a diol such as ethylene glycol, tetramethylene glycol, 1,6-hexane diol, neopentyl glycol, 1,4-butane diol, or the like. As examples of the polycarbonate diol, a polycarbonate diol of 20 polytetrahydrofuran, polycarbonate of 1,6-hexane diol, and the like are given. These polycarbonate diols are commercially available under the trademarks DN-980, DN-981, DN-982, DN-983 (manufactured by Nippon Polyurethane Industry Co., Ltd.), PC-8000 (manufactured by PPG in US), and the like. Given as examples of the diamine are diamines such as ethylenediamine, tetramethylenediamine, hexamethylenediamine, p-phenylene diamine, 4,4'-diamino diphenylmethane, diamines including a hetero atom, and polyether 25 diamines.

The aforementioned polyisocyanate (b) is a compound containing 2-6 isocyanate groups with diisocyanates being preferred. Specific examples of the polyisocyanate (b) include 2,4-tolylene diisocyanate, 5 2,6-tolylene diisocyanate, 1,3-xylene diisocyanate, 1,4-xylene diisocyanate, 1,5-naphthalene diisocyanate, p-phenylene diisocyanate, 3,3'-dimethyl-4,4'-diphenylmethane diisocyanate, 4,4'-diphenylmethane diisocyanate, 3,3'-dimethylphenylene diisocyanate, 10 4,4'-biphenylene diisocyanate, hexamethylene diisocyanate, isophorone diisocyanate, dicyclohexylmethane diisocyanate, methylenebis(4-cyclohexylisocyanate), hydrogenated diphenylmethane diisocyanate, 2,2,4-trimethylhexamethylene diisocyanate, 15 bis (2-isocyanatoethyl) fumarate, 6-isopropyl-1,3-phenyl diisocyanate, 4-diphenylpropane diisocyanate, and lysine diisocyanate.

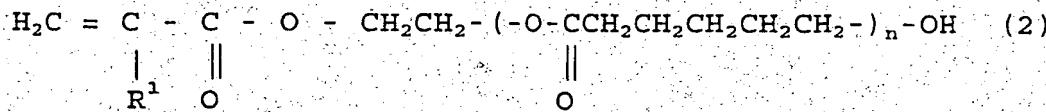
The above-noted compound (c) having an active hydrogen and a polymerizable unsaturated group, 20 may include, for example, (meth)acryl type compounds having at least one hydroxyl group. Specific examples of the compound (c) include 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 2-hydroxyoctyl (meth)acrylate, pentaerythritol 25 tri(meth)acrylate, glycerol di(meth)acrylate, dipentaerythritol monohydroxy penta(meth)acrylate, 1,4-butanediol mono(meth)acrylate, 4-hydroxycyclohexyl (meth)acrylate, 1,6-hexanediol mono(meth)acrylate, neopentyl glycol mono(meth)acrylate, trimethylolpropane 30 di(meth)acrylate, trimethylolethane di(meth)acrylate,

and (meth)acrylates represented by the following formulae (1) and (2):



wherein R^1 represents a hydrogen atom or a methyl group;

10



15 wherein R^1 is the same as defined above and n denotes an integer from 1 to 5. Among these groups, 2-hydroxyethyl (meth)acrylate is given as a preferable example.

Polymer (A) may be prepared by reacting at 20 least on polyol (a) with at least one polyisocyanate (b) and at least one compound (c) in accordance with procedures and in proportions known for forming such reactions. As for the polymer (A) forming reaction of the polyether polyol (a) with the polyisocyanate (b), 25 and the compound (c), for example, when a diol compound is reacted with a diisocyanate compound and a compound having an ethylenic unsaturated group, it is desirable to use a urethanization catalyst such as copper naphthanate, cobalt naphthanate, zinc naphthanate, 30 dibutyltin dilaurate, triethyl amine, 1,4-diazabicyclo[2.2.2]octane, 2,6,7-trimethyl-1,4-diazabicyclo[2.2.2]octane, or the like in an amount of

0.01 to 1 part by weight of 100 parts of the total amount of reaction components. This reaction may be carried out at any suitable temperature, typically this reaction is performed at a temperature of 10 to 90°C, 5 and preferably 30 to 80°C.

The polymer which is the component (A) preferably contains a polyether polyol urethane-based polymer. The component (A) may either be composed entirely of a polyether polyol urethane-based polymers 10 or include polyether polyol urethane-based polymers as a major component as well as other polymers corresponding to the component (A). Examples of these other polymers meeting the category of the component (A) include polyester polyol urethane-based polymers, 15 polycaprolactone polyol urethane-based polymers, and the like. When the polyether polyol urethane-based polymer is used in combination with the other polymers, the proportion of the polyalkylene structure in the component (A) is preferably at least 50 but not 20 exceeding 98% by weight, more preferably at least 60 but not exceeding 93% by weight, and most preferably at least 70 but not exceeding 90% by weight. If the proportion of the polyoxyalkylene structure in the component (A) is too small, the modulus of elasticity 25 of the resulting cured product increases at a lower temperature, for example, 0°C or less, which tends to cause the transmission loss of optical fiber when the composition is used as a coating material for optical fibers.

30 The proportionate amount of the component (A) polymer) in the composition of the present

invention is generally from 25 to 75% by weight, and preferably from 40 to 70% by weight. If the proportion of the component (A) is too small, the elongation of the resulting cured product from the composition 5 decreases, whereas if the proportion is too large, the viscosity of the composition increases, whereby the handling characteristics tend to be impaired.

Component (B)

10 The poly-functional monomer used as component (B) in the present invention contains two or more, generally 2-10, and preferably 2-6 polymerizable unsaturated groups. It is desirable to use a (meth)acryloyl group as the polymerizable unsaturated 15 group.

In order for the cured coating composition to attain high breaking strength while maintaining a low modulus of elasticity, the poly-functional monomer will preferably have a comparatively low molecular 20 weight, specifically 800 or less, preferably from 100 to 800, and more preferably from 150 to 600. Given as preferable examples of such a poly-functional monomer include di, tri, and tetra(meth)acrylates, with di and tri(meth)acrylates being preferred, and those having a 25 mw of 800 or less being particularly preferred, such as trimethylolpropane tri(meth)acrylate, pentaerythritol (meth)acrylate, ethylene glycol di(meth)acrylate, tetraethylene glycol di(meth)acrylate, polyethylene glycol di(meth)acrylate, 1,4-butanediol 30 di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, 1,9-nonane diol di(meth)acrylate, neopentyl glycol

di(meth)acrylate, trimethylolpropane trioxyethyl (meth)acrylate, tris(2-hydroxyethyl) isocyanuratetri(meth)acrylate, tris(2-hydroxyethyl) isocyanuratedi(meth)acrylate, tricyclodecane 5 dimethanoldi(meth)acrylate, epoxy(meth)acrylate produced by adding a (meth)acrylate to diglycidyl ether of bisphenol A, and 3-methyl-1,5-pentane diol diacrylate. Among these, particularly preferred poly-functional monomers include 1,6-hexanediol diacrylate, 10 1,9-nonane diol diacrylate, triethylene glycol diacrylate, trimethylolpropanealkoxy triacrylate and tricyclodecanedimethanol diacrylate. These monomers as the component (B) may be used either singly or in combinations of two or more.

15 These poly-functional monomers are commercially available under the trademarks, for example, HDDA, L-C9A (manufactured by Daiichi Kogyo Seiyaku Co., Ltd.), Yupimer UV, SA1002, SA2007 (manufactured by Mitsubishi Chemical Corp.), 3-EGA, 14- 20 EGA (manufactured by Kyoeisha Co., Ltd.), PHOTOMER4149 (Sun Nopco Co., Ltd.), Viscoat 700 (manufactured by Osaka Organic Chemical Industry Co., Ltd.), KAYARAD R-604, DPCA-20, 30, 60, 120, HX-620, D-310, 330 (manufactured by Nippon Kayaku Co., Ltd.), Aronix M- 25 210, 215, 315, 325 (manufactured by Toagosei Co., Ltd.), A-MPD (Shin-Nakamura Chemical Co., Ltd.), and the like.

It is desirable that the component (B) poly-functional monomers in the composition of the 30 present invention are present in an amount of 0.1 to 10% by weight, and particularly 0.5 to 5% by weight. If

the amount of the component (B) is too small, the breaking strength of the resulting cured product decreases, whereas if the amount is too large, the modulus of elasticity of the cured product is 5 exceedingly high and the elongation of the cured product decreases, indicating that such a composition is not suitable as a primary coating material for optical fibers.

10 Component (C)

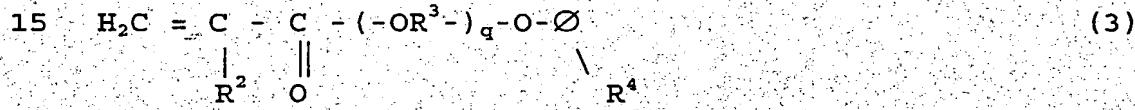
Polymerizable unsaturated group containing monomers suitable as component (C) in the coating composition of the present invention include, for example, monomers possessing only one polymerizable 15 unsaturated group, such as a vinyl group, and a molecular weight of 1,000 or less, and preferably from 70 to 800. Although there are no limitations to the kind of polymerizable vinyl group, it is desirable that a (meth)acryloyl group, N-vinyl group, (meth)acrylamide group, vinyl ether group, vinyl ester group, or the like be contained as the polymerizable vinyl group. 20 Among these, a (meth)acryloyl group is desirable.

Component (C) functions as a reactive diluent in the composition of the present invention and hence it is desirable that component (C) be liquid at 25°C. The types and amounts of compounds used as component (C) are adjusted to control the viscosity of the composition and the modulus of elasticity of the resulting cured product. If component (C) is composed 30 of a plurality of compounds, the selected compounds are

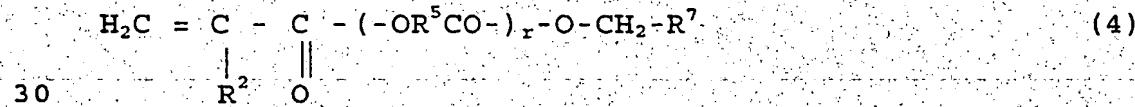
preferably liquids when mixed and result in a mixture that is liquid at 25°C.

Specific examples of suitable monomers for use as component (C) include 2-hydroxyethyl(meth)-5 acrylate, 2-hydroxypropyl(meth)acrylate, 2-hydroxybutyl(meth)acrylate, methyl(meth)acrylate, ethyl(meth)acrylate, propyl(meth)acrylate, isopropyl(meth)acrylate, butyl(meth)acrylate, amyl(meth)acrylate, isobutyl(meth)acrylate, t-butyl-10 (meth)acrylate, pentyl(meth)acrylate, isoamyl(meth)acrylate, hexyl(meth)acrylate, heptyl(meth)acrylate, octyl(meth)acrylate, iso-octyl(meth)acrylate, 2-ethylhexyl(meth)acrylate, nonyl(meth)acrylate, decyl(meth)acrylate, iso-15 decyl(meth)acrylate, undecyl(meth)acrylate, dodecyl(meth)acrylate, lauryl(meth)acrylate, octadecyl(meth)acrylate, stearyl(meth)acrylate, tetrahydrofurfuryl(meth)acrylate, butoxyethyl(meth)acrylate, ethoxydiethylene glycol-20 (meth)acrylate, benzyl(meth)acrylate, cyclohexyl(meth)acrylate, phenoxyethyl(meth)acrylate, polyethylene glycol mono(meth)acrylate, polypropylene glycol mono(meth)acrylate, methoxy ethylene glycol (meth)acrylate, ethoxyethyl(meth)acrylate, 25 methoxypolyethylene glycol (meth)acrylate, methoxypolypropylene glycol (meth)acrylate, dicyclopentadienyl(meth)acrylate, dicyclopentanyl(meth)acrylate, dicyclopentenyl(meth)acrylate, 30 tricyclodecanyl(meth)acrylate, isobornyl(meth)acrylate, bornyl(meth)acrylate, diacetone(meth)acrylamide,

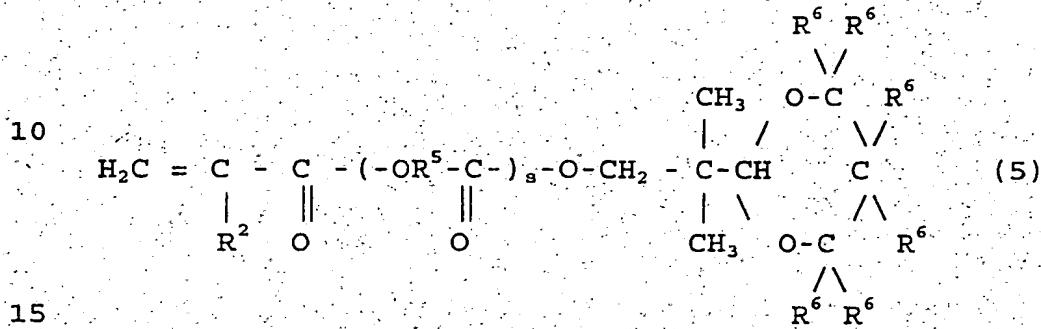
isobutoxymethyl (meth)acrylamide, N-vinylpyrrolidone, N-vinylcaprolactam, N-vinylformaldehyde, N,N-dimethyl (meth)acrylamide, t-octyl (meth)acrylamide, dimethylaminoethyl (meth)acrylate, 5 diethylaminoethyl (meth)acrylate, 7-amino-3,7-dimethyloctyl (meth)acrylate, N,N-diethyl (meth)acrylamide, N,N'-dimethylaminopropyl (meth)acrylamide, (meth)acryloylmorpholine, hydroxybutyl vinyl ether, 10 lauryl vinyl ether, cetyl vinyl ether, vinyl ethers such as 2-ethylhexyl vinyl ether, maleates, fumarates, and the compounds represented by the following formulae (3) to (5):



20 wherein R^2 represents a hydrogen atom or a methyl group, R^3 independently represents an alkylene group having 2-6, and preferably 2-4 carbon atoms, R^4 being attached to the aromatic ring (\emptyset), represents a hydrogen atom or an alkyl group having 1-12, and 25 preferably 1-9 carbon atoms, and q denotes an integer from 0 to 12, and preferably from 1 to 8.



wherein R^2 is the same as defined above, R^5 independently represents an alkylene group having 2-8, and preferably 2-5 carbon atoms, and r denotes an integer from 1 to 8, and preferably from 1 to 4, and R^7 represents a tetrahydrofuryl group.



wherein R^2 and R^5 are the same as defined above, s denotes an integer from 1 to 15, and each R^6 independently represent a hydrogen atom or a methyl group.

Given as examples of compounds represented by formula (3) are nonylphenol EO-modified (8 mols) acrylate, phenol EO-modified (4 mols) acrylate, 25 nonylphenol EO-modified (4 mols) acrylate, nonylphenol PO-modified (2.5 mols) acrylate, nonylphenol EO-modified (1 mol) acrylate, and phenol EO-modified (2 mols) acrylate.

The above exemplified compounds may be used 30 independently or in combinations of two or more.

Among the above exemplified compounds, preferred compounds for use as component (C) include N-vinyl lactams such as N-vinyl pyrrolidone, N-vinyl- ϵ -caprolactam (hereinafter called "N-vinyl caprolactam"), 35 and the like. It is preferred that component (C)

include, relative to component (C), N-vinylcaprolactam in a range of 3 to 20% by weight, and preferably 3 to 15% by weight.

It is desirable that the component (C) 5 contain a compound having an alicyclic structure because the resulting cured product has water resistance, hot water resistance, acid resistance, alkali resistance, and the like and has improved long-term reliability. Examples of such a monomer having an 10 alicyclic structure, particularly, alicyclic (meth)acrylate compounds, include isobornyl (meth)-acrylate, dicyclopentenyl (meth)acrylate, tricyclodecanyl (meth)acrylate, cyclohexyl (meth)acrylate, 15 tricyclodecanedimethanol di(meth)acrylate, and the like.

Among these, isobornyl acrylate and tricyclodecanedimethanol diacrylate are desirable.

In a preferred embodiment, component (C) includes a combination of N-vinyl lactams and compound 20 having an alicyclic structure.

Monomers suitable for use in component (C) are commercially available under the trademarks, for example, Aronix M-102, M-111, M-113, M-114, M-117 (manufactured by Toagosei Co., Ltd.), KAYARAD TC110S, 25 R629, R644 (manufactured by Nippon Kayaku Co., Ltd.), Viscoat 3700 (Osaka Organic Chemical Industry Co., Ltd.) and the like.

It is desirable that component (C) be present in an amount of 20 to 70% by weight, and 30 preferably 25 to 55% by weight relative to the composition of the present invention.

Component (D)

Examples of radiation-active initiators suitable for use as component (D) in the present invention include 1-hydroxycyclohexyl phenyl ketone, 5 2,2-dimethoxy-2-phenylacetophenone, xanthone, fluorenone, benzaldehyde, fluorene, anthraquinone, triphenylamine, carbazole, 3-methylacetophenone, 4-chlorobenzophenone, 4,4'-dimethoxybenzophenone, 4,4'-diaminobenzophenone, Michler's ketone, benzoin propyl 10 ether, benzoin ethyl ether, benzyl methyl ketal, 1-(4-isopropylphenyl)-2-hydroxy-2-methylpropan-1-one, 2-hydroxy-2-methyl-1-phenylpropan-1-one, thioxanthone, diethylthioxanthone, 2-isopropylthioxanthone, 2-chlorothioxanthone, 2-methyl-1-[4-(methylthio)phenyl]- 15 2-morpholino-propan-1-one, 2,4,6-trimethylbenzoyl diphenylphosphine oxide, bis(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentyl phosphine oxide, and the like. These compounds may be used either singly or in combinations of two or more. Among these compounds, 20 2,4,6-trimethylbenzoyl diphenylphosphine oxide, bis(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentyl phosphine oxide, and 1-hydroxycyclohexyl phenyl ketone are desirable.

Examples of commercially available products suitable for use as component (D) include Irgacure 184, 25 651, 500, 907 (manufactured by Ciba Speciality Chemicals Co., Ltd.), Lucirin LR8728, Lucirin LR8953X (manufactured by BASF), Darocur E1116, 1173 (manufactured by Ciba Speciality Chemicals Co., Ltd.), 30 and Ubecryl P36 (manufactured by UCB Co.).

Component (D) may include one or more radiation-active initiator. The proportion of component (D) in the composition of the present invention is generally from 0.1 to 10% by weight, and preferably from 1 to 5% by weight, relative to the total weight of the composition.

A photoinitiator agent may also be used as required by the particular application in addition to the radiation-active initiators present as component (D). Given as suitable examples of photoinitiators are triethylamine, diethylamine, N-methyldiethanoleamine, ethanolamine, 4-dimethylaminobenzoic acid, ethyl 4-dimethylaminobenzoate, isoamyl 4-dimethylaminobenzoate, and the like. These compounds are commercially available under the trademarks, for example, of Ubecryl P102, 103, 104, 105 (manufactured by UCB Co.) and the like.

Other components

In addition, depending the particulars of the end use for the composition, it may be preferred to employ ingredients in addition to components (A) to (D). Given as typical examples of such additional ingredients are antioxidants, UV absorbers, light stabilizers, silane coupling agents, aging preventives, thermal polymerization inhibitors, leveling agents, colorants, surfactants, preservatives, plasticizers, lubricants, solvents, fillers, wettability improvers, coating surface improvers, and the like. As examples of antioxidants, phenol type antioxidants, organic sulfur type antioxidants, and the like are given. These

antioxidants are commercially available under the trademarks, for example, Irganox1010, 1035, 1076, 1222 (manufactured by Ciba Speciality Chemicals Co., Ltd.) and the like.

5 As examples of UV-absorbers, benzotriazole type UV-absorbers and the like are given. Examples of commercially available products used as the UV absorbers include Tinuvin P, 234, 320, 326, 327, 328, 213 (manufactured by Ciba-Geigy), Sumisorb 110, 130, 10 140, 220, 250, 300, 320, 340, 350, 400 (manufactured by Sumitomo Chemical Industries Co., Ltd.), and the like.

As examples of light stabilizers, hindered amine type light stabilizers and the like are given.

Examples of commercially available products of the 15 light stabilizers include Tinuvin 292, 144, 622LD (manufactured by Ciba Speciality Chemicals Co., Ltd.), Sanol LS-770, 765, 292, 2626, 1114, 744 (manufactured by Sankyo Chemical Co.), and the like.

Examples of compounds used as silane 20 coupling agents include γ -aminopropyltrimethoxysilane, γ -mercaptopropyltrimethoxysilane, γ -methacryloxypropyltrimethoxysilane, and commercially available products such as SH6062, SZ6030 (manufactured by Toray-Dow Corning Silicone Co.), KBE903, KBM803 25 (manufactured by Shin-Etsu Silicone Co., Ltd.), and the like. As examples of aging preventive agents, phenol type, allyamine type, and ketone amine type aging preventive agents are given. Examples of commercially available products of the aging preventives include 30 Antigene W, S, P, 3C, 6C, RD-G, FR, AW (manufactured by Sumitomo Chemical Industries Co., Ltd.), and the like.

The composition of the present invention can be prepared by formulating the aforementioned components (A) to (D) and components added as required in prescribed amounts respectively.

5 The viscosity at 25°C of the resulting composition is preferably from 1,000 to 20,000 cp, and more preferably from 1,500 to 15,000 cp, to ensure excellent coatability on optical fibers.

10 The composition of the present invention is radiation-curable so that it can be cured by exposure to appropriate radiation. Here, radiation source includes infrared light, visible rays, ultraviolet light, α -rays, β -rays, γ -rays, and the like. When the composition is cured, for example, by exposure to 15 ultraviolet light, it can be cured at a dose of 2 to 2000 mJ/cm^2 , preferable 50-200 mJ/cm^2 .

Utility

20 The composition of the present invention are suitable for many uses including, for example, as a paint, surface reforming material, printing ink, and coating material for substrates, in particular optical fibers.

25 Among the cured products produced by irradiating with ultraviolet light at a dose of 1 J/cm^2 in air, those at a thickness of 200 μm cured coating having a secant modulus (prescribed in JIS K 7127) of 0.15 kg/mm^2 or less, more preferably 0.1 to 0.05 kg/mm^2 and a tensile strength at break 30 (prescribed in JIS K 7127) of more than 0.15 kg/mm^2 , more preferably 0.25 kg/mm^2 to 0.50 kg/mm^2 , are

preferably used as a primary coating for optical fibers since these possess an appropriate modulus of elasticity and excellent breaking strength when these are used as a primary coating for optical fibers. In order to obtain coated optical glass fibers with good handling properties, it is preferred to have the glass fiber which is coated with an adhering primary coating, further coated with a harder secondary coating.

10 A coating layer of the composition in accordance with the present invention can have a thickness in the range of 5 to 500 μm , preferably 15 to 300 μm . A primary coating for optical glass fibers generally has a thickness of about 30 μm (15-15 50 μm).

15 In a preferred form of the composition of the present invention, the composition comprises components (A), (B), (C), and (D) in ranges, relative to the total weight of the composition, of 20 from 25 to 75% by weight, from 0.1 to 10% by weight, from 20 to 70% by weight, and 0.1 to 10% by weight, respectively. Preferred composition of the present invention include those having a viscosity of 1,000 to 20,000 at 25°C. The composition of the present 25 invention is preferably adapted for use as a primary coating for optical fibers.

EXAMPLES

30 The present invention will be explained in more detail by way of examples, which are not intended to be limiting of the present invention. In

the examples hereinafter "part(s)" indicates "part(s) by weight" unless otherwise described.

Synthesis Example 1

5 Synthesis of a polymer for component (A)

4.07 g of tolylene diisocyanate (including 97.5% by weight or more of a 2,4-derivative and 2.5% by weight or less of a 2,6-derivative), 59.3 g of a ring-opening copolymer of ethylene oxide and tetrahydrofuran 10 having a number average molecular weight (hereinafter abbreviated as "Mn") of 4,000, 0.02 g of 2,6-di-t-butyl-p-cresol, and 0.007g of phenothiazine were placed in a reaction vessel equipped with a stirrer. This mixture was cooled with ice until the temperature of 15 the mixture was 10°C or lower while stirring. When the temperature was 10°C or lower, 0.08 g of dibutyltin dilaurate was added to the mixture, followed by stirring for 2 hours, while controlling the liquid temperature at 20 to 30°C. Then, 0.33 g of γ -mercaptopropyltrimethoxysilane (trademark: SH6062, 20 manufactured by Toray-Dow Corning Silicone Co., Ltd.), which is a silane coupling agent, was added and the mixture was stirred at 40 to 50°C for one hour. After the stirring was completed, 1.15 g of 2-hydroxyethyl acrylate was added and the resulting mixture was 25 stirred at a liquid temperature of 45 to 55°C for 30 minutes.

Next, 0.13 g of methanol was added to the reaction solution, which was continuously stirred at 55 30 to 60°C for four hours. The reaction was terminated when the residual isocyanate was 0.1% by weight or less to

obtain a liquid urethane acrylate polymer with a Mn of 8,327, which corresponded to the component (A).

Examples 1 to 5 and Comparative Examples 1 and 2

5 10 g of lauryl acrylate, 17 g of polyoxyethylene nonyl phenyl ether acrylate (trademark: M113, manufactured by Toagosei Co., Ltd.), 5 g of N-vinylcaprolactam, 0.8 g of Irganox 1035 as an antioxidant, 2 g of 2,4,6-trimethylbenzoyl

10 diphenylphosphine oxide, and 0.15 g of diethylamine were added to 65 g of the liquid urethane acrylate polymer prepared in Synthetic Example 1. The mixture was stirred, while controlling the temperature at 50 to 60°C, until a uniform and transparent liquid was

15 prepared to obtain a resin solution I.

In Examples 1 to 5, 100 parts of the resin solution I and each of the poly-functional monomers shown in Table 1 in the amount shown in Table 1 were placed in a reaction vessel equipped with a stirrer to 20 prepare a composition. The mixture was stirred for 3 hours while controlling the temperature at 50 to 60°C. The viscosity of each of the resulting compositions was measured by a B-type viscometer at 25°C. The results are shown in Table 2. The viscosity of each of all 25 compositions was in a range from 5,000 to 6,000 cp. In Comparative Example 1, the resin solution I was used as it was without using a poly-functional monomer.

Table 1

	(B) Poly-functional monomer (parts)	Viscosity (cp/25°C)
Example 1	1,6-hexanediol diacrylate (1.5)	5500
Example 2	1,9-nonenediol diacrylate (3.0)	5400
Example 3	Triethylene glycol diacrylate (1.0)	5500
Example 4	Tricyclodecanedimethanol diacrylate (3.0)	5400
Example 5	Trimethylolpropane-alkoxy triacrylate (2.0)	5500
Comp. Example 1	-	5500
Comp. Example 2	Lauryl acrylate (2.5)	5400

Each of the compositions prepared in this manner was applied to the surface of a glass plate using an applicator for 250 μ m thickness and was irradiated with ultraviolet light at a dose of 1.0 J/cm² in air using a 3.5 kW metal halide lamp (SMX-3500/F-OS, manufactured by ORC Co., Ltd.) to obtain a cured film with a thickness of 200 μ m. The cured film was then cut into strip specimens of 0.6 cm width to make a test sample. The condition of the test sample was appropriately adjusted at 23°C under a humidity of 50% for 12 hours or more and then subjected to measurements of modulus of elasticity and breaking strength illustrated below. The results are shown in Table 2.

Measurement of modulus of elasticity

The secant modulus was measured in the conditions of a tension speed of 1 mm/minute and an interval between bench marks of 25 mm according to JIS 5 - K7127.

Measurement of breaking strength

The tensile strength at break was measured in the conditions of a tension speed of 50 mm/minute and an interval between bench marks of 25 mm at 23°C under a humidity of 50%RH according to JIS K7127.

Table 2

	Secant modulus (kg/mm ²)	Tensile strength at break (kg/mm ²)
Example 1	0.06	0.48
Example 2	0.07	0.42
Example 3	0.06	0.37
Example 4	0.08	0.34
Example 5	0.10	0.28
Comp. Example 1	0.04	0.06
Comp. Example 2	0.04	0.05

As is clear from Tables 1 and 2, each of the compositions of Examples 1 to 5 had a viscosity of an appropriate range for coating optical fibers and the resulting cured product exhibited a tensile strength at break as high as 0.26 to 0.42 kg/mm² while its secant modulus was as low as 0.06 to 0.11 kg/mm². On the other hand, the cured film prepared from the compositions of

Comparative Examples 1 and 2 excluding the poly-functional monomer had a low tensile strength at break.

It is apparent from the aforementioned 5 explanations that the radiation curable composition of the present invention is featured in that the cured product possesses a high breaking strength while its modulus of elasticity is low. Hence, when the radiation curable composition is used as a coating material for 10 optical fibers, it can protect optical fibers for a long period of time in a safe and stable manner while an excellent optical transmission performance is maintained.

WHAT IS CLAIMED IS:

1. A coated optical fiber comprising:
 - 5 a coating having,
 - a tensile strength at break of more than 0.15 kg/mm², and
 - 10 a secant modulus of 0.15 kg/mm² or less.
2. The coated optical fiber according to claim 1,
 - 10 wherein the coating is formed from a radiation-curable composition comprising:
 - (A) a polymer composition comprising one or more polymers having,
 - 15 i) urethane bonds in a molecular chain, and
 - ii) a number average molecular weight of 3,000-30,000,
 - 20 wherein the composition has on average 1.2 or more polymerizable unsaturated groups per polymer molecule;
 - (B) a poly-functional monomer having two or more polymerizable unsaturated groups;
 - (C) a monomer having one polymerizable unsaturated group; and
 - 25 (D) a radiation-active initiator.
 3. The coated optical fiber of claim 2, wherein the polymer composition (A) comprises a polyether polyol urethane-based polymer.
 4. The coated optical fiber according to any one of claims 2-3, wherein the polymer composition (A)

comprises a polymer derived from a polyoxyalkylene polyether polyol.

5. The coated optical fiber according to any one of claims 2-4, wherein the polymer composition includes at least one polymer having 2-10 urethane bonds.
10. The coated optical fiber according to any one of claims 2-5, wherein the radiation-curable composition comprises, relative to the total radiation-curable composition, between 40 and 70% wt of the polymer composition (A).
15. The coated optical fiber according to any one of claims 2-6, wherein the poly-functional monomer (B) has a molecular weight of 800 or less.
20. The coated optical fiber according to any one of claims 2-7, wherein the radiation-curable composition comprises relative to the total radiation-curable composition, between 0.1 and 10 wt.% of polyfunctional monomer (B).
25. The coated optical fiber according to any one of claims 2-8, wherein the monomer (C) comprises a polymerizable vinyl group.
30. A radiation curable resin composition, comprising:
 - (A) a polymer composition having 1.2 or more polymerizable unsaturated groups on average in one molecule, urethane bonds in a molecular chain, and a number average molecular weight of 3,000-30,000;
 - (B) a poly-functional monomer having a two or more polymerizable unsaturated groups;

(C) a monomer having one polymerizable unsaturated group; and

(D) a radiation-active initiator, wherein the radiation-curable resin composition is irradiated with ultraviolet light in air at a dose of 1 J/cm² to provide a cured product having at a thickness of 200 μm a secant modulus of 0.15 kg/mm² or less and a tensile strength at break of more than 0.15 kg/mm².

10 11. The coating composition according to claim 10, wherein the radiation-curable composition has a viscosity, at 25°C, of from 1,000 to 20,000 cp.

15 12. The coating composition according to any one of claims 10-11, wherein the cured product has a secant modulus of 0.05-0.1 kg/mm², and a tensile strength at break of 0.25-0.5 kg/mm².

13. A coated optical fiber having a primary coating according to any one of claims 1-9 adhering to the glass substrate.

20 14. A coated optical fiber according to claim 13 further having a secondary coating adhering to the primary coating.

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/NL 98/00464A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C03C25/02

According to International Patent Classification(IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 97 19898 A (DSM NV ;JAPAN SYNTHETIC RUBBER CO LTD (JP); ISHIKAWA MIYUKI (JP);) 5 June 1997 see page 7, line 20 - line 35; claims 1,6 ---	1-14
X	WO 96 17000 A (DSM NV) 6 June 1996 see page 15, line 26 - line 32; claims ---	1-14
X	EP 0 336 653 A (UVEXS INC) 11 October 1989 see page 4, line 37 - line 57 ---	1-14
X	EP 0 301 733 A (MITSUI TOATSU CHEMICALS) 1 February 1989 see claims; examples 3,4 ---	1-14
X	EP 0 111 280 A (DESOTO INC) 20 June 1984 see page 5, line 1 - line 26; claims; examples ---	1-14 -/-

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 2 163 755 A (YOKOHAMA RUBBER CO LTD) 5 March 1986 see the whole document	1-14
P,X	WO 98 32780 A (KIKUCHI TOSHIKAZU ;HIRAI TSUYOSHI. (JP); JSR CORP (JP); KOMIYA ZEN) 30 July 1998 see page 9, line 11 – line 23; claims	1-14

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/NL 98/00464

Patent document cited in search report	Publication date		Patent family member(s)	Publication date
WO 9719898	A 05-06-1997		JP 9143233 A AU 7591396 A EP 0863854 A	03-06-1997 19-06-1997 16-09-1998
WO 9617000	A 06-06-1996		AU 691356 B AU 3883195 A CA 2206120 A EP 0794971 A	14-05-1998 19-06-1996 06-06-1996 17-09-1997
EP 0336653	A 11-10-1989		US 4973611 A AU 3235389 A JP 1299812 A	27-11-1990 05-10-1989 04-12-1989
EP 0301733	A 01-02-1989		JP 1024816 A AU 590483 B	26-01-1989 02-11-1989
EP 0111280	A 20-06-1984		US 4932750 A CA 1198083 A	12-06-1990 17-12-1985
GB 2163755	A 05-03-1986		JP 1760958 C JP 4049867 B JP 61014210 A	20-05-1993 12-08-1992 22-01-1986
WO 9832780	A 30-07-1998		JP 10204250 A AU 5578998 A	04-08-1998 18-08-1998